

SPECIFICATION

Attorney Docket No. 05331.00002

TO ALL WHOM IT MAY CONCERN:

Be it known that Donald C. Young, a citizen of the United States and a resident of Fullerton, California, has invented certain new and useful improvements in an

AMMONIUM PHOSPHATE/PHOSPHITE FERTILIZER COMPOUND

of which the following is a specification.

BACKGROUND OF THE INVENTION

In a principal aspect the present invention comprises a generally neutral, liquid phosphorus containing fertilizer having a significant phosphite ion concentration. Phosphorus acid, ammonia and water properly mixed pursuant to controlled temperature and pH conditions produce a stable phosphite ion containing solution which may be mixed with other fertilizer materials including ammonium phosphates. The invention further relates to methods for preparing such fertilizers and the use of such fertilizers on plants.

Nitrogen, phosphorus and potassium are principal elements found in fertilizer compositions applied as solutions or in granular form to enhance plant growth. A great deal of research and development has focused upon maximizing the efficacious delivery of these elements to plant life. Various compositions incorporating these elements have been patented. For example, Hsu in U.S. Pat. No. 5,707,418 discloses an inorganic phosphorus containing fertilizer comprised of various phosphorus compounds in the form of acids or salts in combination with an inorganic complexing agent. The purpose of the Hsu invention is to provide a highly stable, concentrated phosphorus containing fertilizer, which can be stored for long periods of time yet easily absorbed through the foliage system or the root system of a plant and a process for manufacturing the material. Hsu in U.S. Pat. 5,865,870 discloses a phosphorus containing fertilizer, which is a combination of polyphosphoric acid and salts and phosphorous acid, with the goal of obtaining increased phosphorus uptake by plants exposed to this fertilizer. Lovatt, in a series of patents including Pat. No. 5,514,200 and Pat. No. 6,113,665 discloses concentrated phosphorus containing fertilizers that employ buffered compositions or defined

mixtures of phosphorus compounds in order to supply phosphorus to plants thereby enhancing phosphorus uptake.

Other patents and publications which relate to such compositions, their manufacture and use, including the following: U.S. Pat. No. 5,890,837; U.S. Pat. No. 5,830,253; U.S. Pat. No. 5,864,418; and *Fertilizer Research* 32, 161-168 (1992).

Reported research indicates that delivery of the phosphorus element to plant life may be effected by exposure to either a phosphate ion (e.g. $\text{H}_2\text{PO}_4^{-1}$) or a phosphite ion (e.g. $\text{H}_2\text{PO}_3^{-1}$). Phosphite ion exposure appears to have an advantage when applied in a solution form to the foliation of a plant because it is more readily assimilated than a phosphate ion. Additionally, combinations of phosphite and phosphate ions are believed to be more effective than either alone in plant assimilation and in providing an effective means for controlling plant fungus diseases.

Providing phosphite ion containing fertilizers constitutes a significant challenge. Formulations of phosphite ion containing materials that have been previously suggested as fertilizers are phosphorous acid (H_3PO_3), and potassium phosphite, (K_2HPO_3). However, phosphorous acid is a stronger acid than phosphoric acid and is highly corrosive thus diminishing its desirability as a phosphite ion source. Potassium phosphite is an expensive compound typically made by neutralizing phosphorous acid with potassium hydroxide. The reaction is highly exothermic. The heat evolved is a challenging problem since phosphorous acid is very unstable. That is, as phosphorous acid is heated above 180° centigrade, then phosphine, PH_3 , is produced. Phosphine is a highly toxic gas that is spontaneously flammable in air.

As a consequence there is a need for a low cost, safe, efficacious source of phosphorous in the form of a phosphite ion (HPO_3^{-2} , $\text{H}_2\text{PO}_3^{-1}$) that is stable, having neutral or nearly neutral

pH and preferably in combination with a nitrogen source. Further, it is desirable to have such a material which can be manufactured utilizing present day, available fertilizer production facilities.

SUMMARY OF THE INVENTION

Briefly, the present invention comprises a phosphorus containing fertilizer composition which includes a significant phosphite ion concentration, and in a preferred embodiment, nitrogen and phosphate ions in the form of ammonium phosphates and polyphosphates. The fertilizer is in the form of a concentrated liquid solution which may be diluted, mixed with other plant growth constituents such as urea, etc., and has a pH when in water solution in the range of about 5 to 8, preferably in the range of about 5.5 to 6.5 or about 6.2. In the preferred embodiment, the composition has a nitrogen concentration in weight percent of about 6 to 10 and a phosphorus concentration in weight percent in the form of P_2O_5 of about 22 to 36. A preferred process for manufacture of the composition utilizes slightly modified ammonium phosphate fertilizer manufacturing facilities to combine phosphorous acid, ammonia and water under controlled conditions of maintaining the temperature below 150°F and the pH generally neutral during batch or continuous process mixing. Mixtures of manufactured ammonium phosphites and species of ammonium phosphates are considered most desirable, particularly when the weight percent of phosphorus (P_2O_5) from the phosphite and phosphate compounds are about equal. A most preferred composition comprises a 9.8-34-0 ammonium phosphite/ammonium phosphate solution. The compositions demonstrate significantly improved phosphorus uptake.

Thus it is an object of the invention to provide an improved phosphorus source fertilizer composition.

Yet another object of the invention is to provide a fertilizer composition having a significant source of phosphorus in the form of a phosphite ion and further including a significant source for nitrogen.

Yet another object of the invention is to provide a fertilizer composition which may be manufactured utilizing currently available ammonium phosphate facilities wherein the composition contains highly concentrated amounts of the phosphite ion.

Another object of the invention is to provide a safe, cost effective, and easily monitored process for the manufacture of a phosphorus containing fertilizer in liquid form which has a high concentration of the phosphite ion.

Another object of the invention is to provide various methods and formulations for the manufacture of a nitrogen/phosphorus containing fertilizer composition wherein the phosphorus portion of the composition is in the form of a phosphite ion in solution and wherein the solution is neutral or nearly neutral.

These and other objects, advantages, and features of the invention will be set forth in the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWING

The single drawing comprises a schematic diagram illustrating the steps and the process of manufacture of the nitrogen/phosphorus fertilizer composition of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As previously noted, a basic object of the invention is to produce a high concentration, stable, neutral pH, or nearly neutral pH, liquid fertilizer solution containing ammonium

phosphite as a phosphite ion source. A further object is to provide a process for producing such a product using conventional ammonium phosphate fertilizer production facilities.

As background, it is noted that phosphorous acid, H_3PO_3 , contains the phosphorus atom in the +4 oxidation state rather than the +5 oxidation state of phosphoric acid, H_3PO_4 . While both acids contain three hydrogen atoms, phosphorous acid contains only two ionizable hydrogen atoms. This results because one hydrogen atom in the phosphorous acid is covalently bonded to the phosphorus atom and does not react with neutralizing agents. In contrast, in phosphoric acid all three hydrogen atoms are ionizable.

On average, phosphorous acid is about five times stronger as an acid than phosphoric acid. Phosphorous acid has about the same acid strength as sulfuric acid. Therefore this increased acid strength may indicate the reason that phosphorous acid as a source of the phosphite ion is more active and better transmutable as a phosphorous source for plants. The adverse impact of being an acid, however, precludes its effective use as a fertilizer.

Investigative research by applicant has shown that a mixture of monoammonium phosphite, $\text{NH}_4\text{H}_2\text{PO}_3$, and diammonium phosphite $(\text{NH}_4)_2(\text{HPO}_3)$ has greater water solubility than either of the salts alone. Thus mixing the two compounds provides a synergistic solubility. Further research by applicant has indicated that maximum water solubility results when there is a measured stoichiometry of $(\text{NH}_4) 1.4 \text{ H } 1.6 \text{ PO}_3$. At this maximum water solubility the solution pH is 6.2 which is very tolerable in an agrarian environment. From this research it was determined that an ammonium phosphite solution containing 9.6% nitrogen (N) and 34 percent phosphite (P_2O_5) could be prepared by mixing ammonia, water and 0-60-0 phosphorous acid under reasonable controlled conditions of temperature and pH. Utilizing these starting materials

simplifies production enabling use of slightly modified ammonium phosphate fertilizer production facilities. Through this method of preparation, creation of a useful ammonium phosphite solution as a source of nitrogen and phosphorous in the form of phosphite ions for agricultural uses is possible.

An alternative product composition containing P_2O_5 (as a combination of phosphite and phosphate ions) comprises a mixture of 50 percent of 10-34-0 ammonium polyphosphate solution and 50 percent 9.6-34-0 ammonium phosphite solution made in accord with the process of the invention. The resulting mixture is a 9.8-34-0 compound and solution having 17 percent of the phosphorus (P_2O_5) derived from phosphate and 17 percent of the phosphorous (P_2O_5) derived from phosphite. The nitrogen is, of course, derived from the ammonia.

The 9.8-34-0 ammonium phosphite/ammonium phosphate solutions or the 9.6-34-0 ammonium phosphite solution can be blended in all proportions with standard 10-34-0 or 8-24-0 fertilizer compounds to produce any phosphate/phosphite ratio. Additionally the created product can be mixed with urea, urea solution, potassium chloride, potassium sulfate and potassium phosphate to provide a desired, stable solution with potassium for plant application. The solutions of the invention thus can be used as substitutes for standard 10-34-0 and 8-24-0 materials commercially available.

The products have been evaluated for stability. They have been stored , exposed to air at temperatures of 95°F for several weeks and mixed with nitrate compounds. No oxidation or other chemical or physical changes have been detected. Thus from a stability viewpoint the products are highly desirable. The following are examples of the manufacturing process as conducted in the laboratory:

Example 1

Laboratory batches of the 9.6-34-0 product were prepared as follows. The quantity of 270 g of water was added to a stirred batch reactor. Then 454 g of 0-60-0 phosphorous acid (Chemgrow Co., Solana Beach, CA) and 76.8 g of anhydrous ammonia were added simultaneously to the reactor over a period of about 20 minutes. The addition rate of the phosphorous acid and the ammonia were adjusted to maintain the pH of the reaction mixture between 5.5 and 6.5. The reaction mixture was cooled with an ice bath to maintain the reaction temperature < 60°C. The resulting product was a clear light green solution with a pH of 6.2 and specific gravity of 1.305 2 @ 20°C. The product has a crystallization temperature of < -7°C (20°F).

Example 2

Laboratory batches of the 8.8-29-0 product were prepared as follows. The quantity of 400g of 8-24-0 ammonium orthophosphate solution and 135 g of water were added to a stirred batch reactor. Then 227 g of 0-60-0 phosphorous acid (Chemgrow Co., Solana Beach, CA) and 38.4 g of anhydrous ammonia were added simultaneously to the reactor over a period of about 20 minutes. The addition rate of the phosphorous acid and the ammonia were adjusted to maintain the pH of the reactor mixture between 5.5 and 6.5. The reaction mixture was cooled with an ice bath to maintain the reaction temperature < 60°C. The resulting product was a clear light green solution with a pH of 6.5 and specific gravity of 1.261 @ 20°C. The product has a crystallization temperature of < -7°C (20°F).

Example 3

Laboratory batches of the 9.8-34-0 product were prepared as follows. The quantity of 400 g of 10-34-0 ammonium orthophosphate/ammonium polyphosphate solution (Western Farm Service Alpaugh production) and 135 g of water were added to a stirred batch reactor. Then 227 g of 0-60-0 phosphorous acid (Chemgrow Co., Solana Beach, CA) and 38.4 g of anhydrous ammonia were added simultaneously to the reactor over a period of about 20 minutes. The addition rate of the phosphorous acid and the ammonia were adjusted to maintain the pH of the reaction mixture between 5.5 and 6.5. The reaction mixture was cooled with an ice bath to maintain the reaction temperature <60°C. The resulting product was a clear light green solution with a pH of 6.2 and specific gravity of 1.293 @ 20°C. The product has a crystallization temperature of < -7°C (20°F). The composition and physical properties of the product are listed in Table 1.

TABLE 1

Product Name: 9.8-34-0 Ammonium phosphate/phosphite Solution

%N:	9.8
% P ₂ O ₅ from Phosphate:	17
%P ₂ O ₅ from Phosphite	17
pH:	6.2 ± .2
Specific Gravity, 68°F:	1.293
Lb./gal:	10.78

<u>Composition</u>	<u>Weight %</u>
10-34-0 Ammonium phosphate solution	50.00
0-60-0 Phosphorous acid	23.33
82-0-0 anhydrous ammonia	5.86
Water	15.81

Example 4

Laboratory batches of the 6.4-34-0 product were prepared as follows. The quantity of 370 g of water was added to a stirred batch reactor. Then 369 g of 0-74-0 polyphosphorous acid (50% H_3PO_3 and 50% $\text{H}_4\text{P}_2\text{O}_5$) and 62.4 g of anhydrous ammonia were added simultaneously for mixing to the reactor over a period of about 20 minutes. The addition rate of the polyphosphorous acid and the ammonia were adjusted to maintain the pH of the reaction mixture between 5.5 and 6.5. The reaction mixture was cooled with an ice bath to maintain the reaction temperature $< 60^\circ\text{C}$. The resulting product was a clear light green solution with a pH of 6.6 and specific gravity of 1.252 @ 20°C . The product has a crystallization temperature of $< -7^\circ\text{C}$ (20°F). The product was blended with an equal weight of 10-34-0 ammonium phosphate to produce a stable solution of composition 8.2-34-0.

During the preparation of ammonium phosphite solutions it is very important to maintain the reaction mixture near neutral pH (5.0 to 7.0) or some phosphite can be oxidized to phosphate. This effect is illustrated by the following examples.

Example 5

The 9.6-34-0 product were prepared as follows. The quantity of 270 g of water was added to a stirred batch reactor. Then 454 g of 0-60-0 phosphorous acid (Chemgrow Co., Solana Beach, California) and 76.8 g of anhydrous ammonia were added simultaneously to the reactor over a period of about 20 minutes. The addition rate of the phosphorous acid and the ammonia were adjusted to maintain the pH of the reaction mixture between 5.5 and 6.5. The reaction mixture was cooled with an ice bath to maintain the reaction temperature $< 60^\circ\text{C}$. The resulting product was a clear light green solution with a pH of 6.2 and specific gravity of 1.305 @ 20°C .

The product has a crystallization temperature of $< -7^{\circ}\text{C}$ (20°F). Analysis of the product by ion chromatography showed that it contained 34.5% P_2O_5 as HPO_3^{2-} .

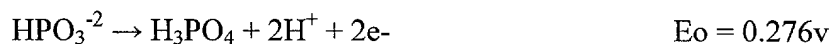
Example 6

The 9.6-34-0 product were prepared as follows. The quantity of 270 g of water and 454 g of 0-60-0 phosphorous acid (Chemgrow Co., Solana Beach, California) were added to a stirred batch reactor. Then 76.8 g of anhydrous ammonia was added to the reactor over a period of about 20 minutes. Control of pH was not regulated. The reaction mixture was cooled with an ice bath to maintain the reaction temperature $< 60^{\circ}\text{C}$. The resulting product was a clear light green solution with a pH of 6.2 and specific gravity of 1.299 @ 20°C . Analysis of the product by ion chromatography showed that it contained 25.4% P_2O_5 as HPO_3^{2-} and 8.5% P_2O_5 as PO_4^{3-} .

Example 7

To demonstrate the stability of phosphite in nitrate solutions under various starting material conditions, a series of tests were conducted.

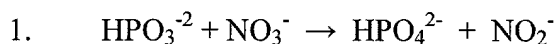
1. It is known that the phosphite ion (HPO_3^{-2}) is a strong reducing agent:



2. Also the nitrate ion (NO_3^-) is a strong oxidizing agent:



The above oxidation-reduction potentials indicate that HPO_3^{-2} will be oxidized by NO_3^- to HPO_4^{2-} according to the following reaction:



However, the kinetics of the reaction is not known. A laboratory study was carried out to measure the stability of $\text{HPO}_3^{-2}/\text{NO}_3^-$ solutions of various types.

The study was conducted by preparing:

1. Solution 1 -- A solution of 25% ammonium nitrate, 40% 9.8-34-0 ammonium phosphite/phosphate solution and 35% water. (Initial composition is 6.8% P_2O_5 as phosphite and 6.8% P_2O_5 as phosphate.)
2. Solution 2 -- A solution of 25% ammonium nitrate, 11.3% 0-60-0 phosphorous acid and 63.7% water. (Initial composition is 6.8% P_2O_5 as phosphite.)

The solutions were each maintained at 20°C (68°F) and analyzed periodically using ion chromatography. Table 2 records the results:

TABLE 2

Time	%P ₂ O ₅ as Phosphite		%P ₂ O ₅ as Phosphate	
	Solution 1	Solution 2	Solution 1	Solution 2
0 hr	6.8	6.8	6.8	Nil
2 hr	6.8	5.9	6.7	0.8
4 hr	6.8	1.2	6.7	5.7
8 hr	6.8	Nil	6.7	6.9
1 day	6.8	Nil	6.7	6.8
10 days	6.8	NA	6.7	NA
28 days	6.8	NA	6.7	NA

*NA: Not Analyzed

The results are surprising for Solution 1. There is no measurable change after 28 days. By contrast, Solution 2 shows the expected rapid oxidation of phosphite to phosphate. The specific composition of 9.8-34-0 significantly reduces the rate of reaction 1 (above) as demonstrated by

the results for solution 1, which is, of course, an embodiment of the invention. This is a great practical advantage since fertilizers containing both phosphite and nitrate can be manufactured, distributed and applied without loss of phosphite.

Manufacturing Process

The process for the manufacture of commercial quantities of the fertilizer is schematically illustrated in the figure. The process may be operated in a batch or a continuous manner. Hourly through put is preferably about equal to the volume of the process container. Preferably the process is maintained and operated in a facility wherein cooling apparatus is provided to maintain the formulation or mixing operations at less than 150°F. Hot spots are to be avoided. Maintaining the temperature below 150°F is deemed important. The ammonium phosphite or the ammonium phosphate/phosphite solutions can be manufactured in any standard 10-34-0 or 8-24-0 plant with such cooling capacity. If the 10-34-0 plant has a pipe reactor or similar high temperature polymerization reactor, this part of the plant must be bypassed by the phosphorous acid stream since it will decompose the phosphorous acid if it does not bypass.

To produce 9.6-34-0 compound, phosphorous acid, ammonia and water are merely added to the reactor and mixed appropriately at the temperature and pH set forth previously. To produce 9.8-34-0 orthopolyphosphoric acid via a polymerization reactor, phosphorus acid, ammonia, and water are added to the reactor. Alternatively, premanufactured 10-34-0 ammonium phosphate, phosphorous acid, ammonia and water are all added to the reactor. However, using premanufactured 10-34-0 ammonium phosphate is not preferred since such use may result in some hydrolysis thereby adversely affecting product stability. To produce 8.8-29-0 compound solution, orthophosphoric acid, phosphorous acid, ammonia and water are added to

the reactor. Alternatively, premanufactured 8-24-0 compound, phosphorous acid, ammonia and water are added to the reactor. The following is an example of commercial production:

Commercial Manufacture Example

The Western Farm Service 10-34-0 plant at Alpaugh, California was modified with an additional line and valves to allow the phosphorous acid, 0-60-0, to be added directly to the mix tank, bypassing the 'pipe reactor'. The Alpaugh 10-34-0 plant was operated to produce about 4,500 gal. of 9.8-34-0 ammonium phosphate/phosphite solution. About 24,320 lb. (2,078 gal.) of 10-34-0 ammonium phosphate from the Western Farm Service inventory and about 7,690 lb. (723 gal.) of water were added to the mix tank and cooling tower. With the mixer and cooling tower operating about 13,743 lb. (1,174 gal.) of 0-60-0 phosphorous acid and about 2,843 lb. (552 gal.) of anhydrous ammonia were added simultaneously over a period of about 90 minutes. During the operation the pH of the reactor solution was maintained between 5.5 and 6.5 by adjusting the ammonia flow. The final pH of the product was adjusted to 6.2. Additional water was added to the final product (to compensate for water lost in the cooling tower) to adjust the final product specific gravity to 1.29. The heat load on the plant is about 50% of the heat load from the production of standard 10-34-0. The reaction temperature during the production was maintained less than 140°F. The final 9.8-34-0 product, a clear light green solution, was transferred to storage. Table 3 shows the recipe for various batch sizes of 9.8-34-0 in a standard 10-34-0 plant:

TABLE 3

Batch Size, Gal Product	Add to Mix Tank			Add Simultaneously. Temp. 150 F Max				Run Time ¹
	10-34-0, gal	Water, gal	Total gal	0-60-0, lb	0-60-0, gal	NH ₃ , lb	NH ₃ , lb	Min.
1000	462.3	204.5	666.8	3054	260.8	631.7	122.7	16.30
1500	693.4	306.8	1000	4581	391.2	947.6	184.0	24.45
2000	924.5	409.0	1334	6108	521.6	1263.4	245.3	32.60
2500	1155.7	511.3	1667	7635	652.0	1579.3	306.7	40.75
3000	1386.8	613.5	2000	9162	782.4	1895.1	368.0	48.90
3500	1617.9	715.8	2334	10689	912.8	2211.0	429.3	57.05
4000	1849.1	818.0	2667	12216	1043	2526.8	490.6	65.20
4500	2080.2	920.3	3000	13743	1174	2842.7	552.0	73.35
5000	2311.3	1022.5	3334	15270	1304	3158.5	613.3	81.50

¹At 16 gal/min. 0-80-0; 7625 gal/min NH₃

Analysis of the product showed it to contain 10.1% nitrogen (Kjeldahl), 16.9% P₂O₅ as phosphate (Ion Chromatography) and 17.2% P₂O₅ as phosphite (Ion Chromatography).

Efficacy Testing

A study was conducted to demonstrate the efficacy of the fertilizer materials of the invention as compared with various controls. Four tests were conducted with the first test

directed to use of a fertilizer of the invention, 9.8-34-0 ammonium phosphate/ammonium phosphite solution. The remaining three tests were directed to the use of various conventional fertilizers.

Procedure

Plastic pots, 5 inches in diameter, were filled with San Joaquin Valley calcareous soil, pH 7.9. The phosphate fertilizer treatments were applied to the soil as a 1 inch band at a depth of 2 inches. Tomato seeds, Early Girl variety, 3 seeds per pot, were planted at a depth of 1 inch. The plants were grown in the greenhouse under standard conditions. The tomato plants were allowed to grow for 30 days (early bloom). The petiole of the fourth leaf from the growing tip was harvested from each plant and analyzed for total phosphorus.

Treatments

All treatments were applied at the rate of 100 pounds per acre, P₂O₅ equivalent.

<u>Treatment Number</u>	<u>Treatment Description</u>
1	9.8-34-0 (ammonium phosphate/ammonium phosphite solution)
2	10-34-0 (ammonium phosphate solution)
3	(NH ₄) ₂ HPO ₃ (diammonium phosphite)
4	K ₂ HPO ₃ (dipotassium phosphite)

Replications

4

Results

<u>Treatment No.</u>	<u>Replication</u>				<u>Mean</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	
1	5660	6111	5100	4100	5243
2	2995	3509	2515	3600	3155
3	3880	3050	2410	3255	3149
4	2517	3525	2695	3512	3062

Treatment 1 was most effective for providing phosphorus to the plant. Treatments 2, 3, and 4 were less effective and there is no statistically significant difference among treatments 2, 3, and 4. The combination of ammonium phosphate and ammonium phosphite is a more effective phosphate fertilizer than either ammonium phosphate, diammonium phosphite or potassium phosphite alone.

In the manufacture of such fertilizer solutions, variance of the constituents from the nominal or preferred amounts (ratios), in the range of ± 10 to 20% by weight is generally considered to be within the scope of the invention. The nominal weight proportions are, of course, preferred for purposes of product shipment. The resulting solution may remain in a concentrated form to be diluted at the application site. Typically, dilution of a solution such as described commercially heretofore in the amount of 10 to 50 times with water is acceptable.

In sum, the methods and compositions of the invention are directed to the production of phosphite, HPO_3^{2-} and $\text{H}_2\text{PO}_3^{1-}$, ions in solution for application as an efficacious fertilizer compound and/or fungicide. The compound has desirable foliage uptake and a desired pH for useful application.

The phosphite compounds disclosed as a source of phosphite ions may be utilized in combination with various nitrogen sources including ammonium phosphate compounds and ammonium nitrate compounds and analogs and derivatives thereof provided appropriate temperature and pH conditions are maintained. The efficacy and stability of such materials is augmented by maintaining the desired ratios of P_2O_5 source approximately equal in the context of phosphite and phosphate source materials. Remarkably, the manufactured phosphite or phosphate/phosphite compositions are stable in the presence of nitrate.

Variations from the disclosed method and composition may be provided without departing from the spirit and scope of the invention. The invention is therefore limited only by the following claims and equivalents thereof.